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(54) OXYGEN-PERMEABLE HARD CONTACT LENS.

(57) An oxygen-permeable hard contact lens obtained by cast-polymerizing a composition composed of 30 to 50 wt. % of alkyl(meth)acrylate, 10 to 40 wt. % of fluorine-containing monomer, 10 to 35 wt. % of silicone (meth)acrylate, 5 to 15 wt. % of unsaturated carboxylic acid, and 0.1 to 15 wt. % of di(meth)acrylate or tri(meth)acrylate of polyhydric alcohol according to a process of continuously or stepwise raising the temperature from 40 to 100°C. and subjecting the resulting product to ordinary machining and abrading to form lens. This lens has excellent staining resistance, flawing resistance, and hydrophilicity.

OXYGEN-PERMEABLE HARD CONTACT LENS

1 TECHNICAL FIELD

This invention relates to an oxygen-permeable hard contact lens. More particularly, it relates to an oxygen-permeable hard contact lens excellent in stain
5 resistance, scratch resistance and hydrophilicity.

BACKGROUND ART

As materials for hard contact lenses polymethylmethacrylate has hitherto been used widely for their excellency in optical properties, physical strength
10 and mechanical processability. However, polymethylmethacrylate has very low oxygen permeability and therefore oxygen supply to ectocornea through these contact lenses can hardly be expected. Accordingly, in case of using these contact lenses for long hours or sleeping
15 with these contact lenses put on, cornea comes to be short of oxygen causing at times congestion, edema and other cornea disorders. Being an avascular tissue, cornea receives supply of the oxygen necessary for metabolism from the oxygen dissolving in lacrima covering
20 the front surface of cornea. Since hard contact lenses generally have a size covering about half the area of cornea, oxygen supply to cornea is made by (a) lacrima exchange at the backside of lens by the pumping action of lens and (b) the lacrima at the cornea part not

1 covered by lens. As a matter of course, it is desirable
for the metabolism of cornea that lens materials them-
selves have high oxygen permeability and, through hard
contact lenses made of these materials, oxygen by
5 supplied to cornea.

In recent years, with a view to replace con-
ventional hard contact lenses mainly composed of
polymethylmethacrylates and to provide lenses capable of
supplying oxygen to cornea through lenses by using lens
10 materials of high oxygen permeability, there have been
disclosed (a) a silicone methacrylate type hard contact
lens, namely, a hard contact lens whose oxygen perme-
ability has been enhanced by introducing a siloxane bond
to the ester portion of a methacrylic acid ester (Japanese
15 Patent Publication No. 33502/1977), (b) an oxygen-
permeable hard contact lens mainly composed of a cellulose
such as cellulose acetate butylate (CAB) and (c) an
oxygen-permeable hard contact lens using a fluorine-
containing methacrylate (Japanese Laid-Open Patne Applic-
20 ation No. 51705/1982). In general, oxygen-permeable hard
contact lenses mainly composed of silicone methacrylates
such as disclosed in Japanese Patne Publication No.
33502/1977, have oxygen permeability higher by several
tens to several hundreds times compared with conventional
25 hard contact lenses mainly composed of polymethyl-
methacrylate, but are usually inferior to them in hardness
and hydrophilicity and further tend to pick up stains of
lipids and the like. Generally, oxygen-permeable hard

1 contact lenses mainly composed of silicone methacrylates
are copolymers between a silicone methacrylate and a
methyl methacrylate and, when the proportion of the
silicone methacrylate becomes higher, these contact
5 lenses will have improved oxygen permeability but reduced
hardness, higher possibility of scratch formation during
handling and worsened polishability. Further, their
hydrophilicity becomes worse and therefore their hydro-
phobicity is increased, and consequently their wettability
10 by water is deteriorated resulting in higher, tendency of
adsorbing up lipids such as lecithin and the like, and
resultantly oxygen-permeable hard contact lenses contain-
ing higher contents of silicone methacrylates are liable
to adsorb stains more easily. Since oxygen-permeable
15 hard contact lenses mainly composed of silicone metha-
crylates have poor wettability by water which is
characteristic of silicone, among these lenses there are
those whose surface have been treated so as to have higher
hydrophilicity. However, this treated surface layer
20 having higher hydrophilicity is as very thin as 1/1000
the lens thickness and accordingly the hydrophilicity
is gradually lost during use of lens necessitating, in
cases, surface retreatment for higher hydrophilicity.

The present inventors previously found out in
25 Japanese Laid-Open Patent Application No. 51705/1982 that
an oxygen-permeable hard contact lens can be obtained
from a copolymer comprising a fluorine-containing monomer.
However, further improvements in oxygen permeability,

1 surface hardness and hydrophilicity have been desired for
this contact lens.

A hard contact lens made of cellulose acetate
butylate is somewhat superior in oxygen permeability and
5 hydrophilicity compared with conventional hard contact
lenses made of polymethylmethacrylate, but has small
hardness and therefore is damaged more easily and
consequently lens parameters are liable to change during
use of the lens.

10 DISCLOSURE OF THE INVENTION

In view of the above circumstances, the present
inventors made extensive studies for development of a
hard contact lens free from the drawbacks of conventional
oxygen-permeable hard contact lenses, having high oxygen
15 permeability, and being excellent in stain resistance,
scratch resistance (surface hardness) and hydrophilicity.
As a result, this invention has been accomplished.

That is, an object of this invention is to
provide an oxygen-permeable hard contact lens excellent
20 in stain resistance, scratch resistance and hydrophilicity.

The oxygen-permeable hard contact lens according
to this invention can be obtained by polymerizing in a
mold a composition composed of 30 to 50% by weight of an
alkyl (meth)acrylate, 10 to 40% by weight of a fluorine-
25 containing monomer, 10 to 35% by weight of a silicone
(meth)acrylate, 5 to 15% by weight of an unsaturated
carboxylic acid and 0.1 to 15% by weight of a di- or

1 tri(meth)acrylate of a dihydric or higher hydric alcohol
by a continuous or stepwise temperature raising method of
40 to 100°C and processing the resulting copolymer into
a lens shape by standard methods of machining and polish
5 ing. The (meth)acrylate in the above description refers
to both acrylate and methacrylate.

BEST MODE FOR CARRYING OUT THE INVENTION

In the oxygen-permeable hard contact lens of
this invention, by using a fluorine-containing monomer
10 such as trifluoroethyl (meth)acrylate, pentafluoroisopropyl
(meth)acrylate or the like and further by adding a silicone
(meth)acrylate to enhance oxygen permeability, not only
oxygen permeability is improved but also hardness is
increased unexpectedly by a synergism with the effect of
15 an crosslinking agent and improvement in the uniformity
of the polymer obtained. Hence, the oxygen-permeable
hard contact lens of this invention is superior in hard-
ness to conventional copolymers of a fluorine-containing
monomer and an alkyl methacrylate and copolymers of a
20 silicone monomer and an alkyl methacrylate, and possesses
remarkably improved scratch resistance. Further, owing
to the effect of the fluorine-containing monomer, the
contact lens of this invention adsorbes stains such as
proteins, lipids and the like present in lacrima, in a
25 less quantity, compared with conventional oxygen-
permeable hard contact lenses mainly composed of silicone
methacrylates.

1 As the fluorine-containing monomer, there are used
perfluoroalkyl methyl (meth)acrylates such as trifluoro-
ethyl (meth)acrylate, pentafluoroisopropyl (meth)-
acrylate, heptafluorobutyl (meth)acrylate, hexafluorois-
5 opropyl (meth)acrylate and the like in a quantity of 10
to 40% by weight. These compounds can be used alone or
in combination of two or more. The effect of the
fluorine-containing monomer is, as aforementioned, to
give the obtained polymer improved uniformity and clarity
10 and enhanced stain resistance together with other
copolymerizable components of this invention and at the
same time to provide increased hardness and accordingly
improved scratch resistance, mechanical processability and
polishability while retaining high oxygen permeability.
15 Particularly improvements in scratch resistance, mechanical
processability and polishability owing to increased hard-
ness were surprisingly high contrary to the level antici-
pated at the early stage. When the fluorine-containing
monomer is used in a quantity less than the range
20 mentioned earlier, the above effect does not appear. When
it is used in a quantity more than the above range, the
hardness of the polymer obtained tends to decrease.
Particularly preferable fluorine-containing monomers are
those having a small molecular weight and possessing a
25 trifluoromethyl group at the end such as trifluoroethyl
(meth)acrylate, hexafluoroisopropyl (meth)acrylate and
the like. Although, in co-polymers of a silicone (meth)-
acrylate and an alkyl (meth)acrylate, as the proportion

1 of the former monomer increases, cloudiness and/or
 striae appear, such cloudiness and/or striae do not
 appear in copolymers of a fluorine-containing monomer
 and an alkyl (meth)acrylate even if the proportion of
 5 the former monomer is increased. Similarly, in copolymers
 of a fluorine-containing monomer, an alkyl (meth)-
 acrylate and a silicone (meth)acrylate, cloudiness
 and/or striae do not appear, and optically uniform and
 clear copolymers are produced. Hence, addition of
 10 the silicone (meth)acrylate as a polymer component is
 very advantageous in improving the oxygen permeability
 of a polymer.

Representative as the alkyl (meth)acrylate are
 methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl
 15 (meth)acrylate, iso-propyl (meth)acrylate, n-butyl
 (meth)acrylate, iso-butyl (meth)acrylate, tert-butyl
 (meth)acrylate, etc. These monomers are used in the
 range of 30 to 50% by weight and enhance mechanical
 processability, polishability and optical stability of
 20 the polymer obtained. The use of methyl (meth)acrylate
 is preferable.

The unsaturated carboxylic acid is a poly-
 merizable monomer containing carboxylic group, and acrylic
 acid and methacrylic acid are representative. This
 25 component has an effect of imparting hydrophilicity to
 contact lens material, and effectively enhances the
 surface hydrophilicity of contact lenses particularly
 when the contact lenses are immersed in water. In the

1 case of using methacrylic acid in this invention, it
has been found out that this acid not only enhances
hydrophilicity but also contributes to increase of
hardness. The unsaturated carboxylic acid is used in
5 a quantity of 5 to 15% by weight. When it is used in
a quantity of less than 5% by weight, sufficient hydro-
philicity can not be obtained. When it is used in a
quantity of more than 15% by weight, the copolymer
obtained has cloudiness and/or brittleness. Preferably
10 methacrylic acid is used. Monomers which have been
known for enhancing hydrophilicity such as 2-hydroxy-
ethyl methacrylate, vinylpyrrolidone, acrylamide,
methacrylamide and the like may further be added.

The silicone (meth)acrylate is a component
15 to be added for further enhancing oxygen permeability.
Examples are tris(trimethylsiloxy)silylpropyloxy-
(meth)acrylate, triphenyldimethyldisiloxanylmethyl-
(meth)acrylate, pentamethyldisiloxanylmethyl(meth)-
acrylate, tert-butyltetramethyldisiloxanylethyl(meth)-
20 acrylate, methyldi(trimethylsiloxy)silylpropylglyceryl-
(meth)acrylate and the like. These compounds each
are a monomer having siloxane bond at the ester portion
of a (meth)acrylic acid ester. Higher siloxane bond
content in monomer and higher degree of branching in
25 siloxane bond gives a higher contribution to oxygen
permeability, but at the same time tends to incur
decrease of hardness. Hence, care must be taken in
selection of monomer and determination of its quantity.

1 The silicone (meth)acrylate is used in a quantity of
10 to 35% by weight but its quantity should be
controlled at a necessary minimum in consideration of
decrease of hardness and higher possibility of staining
5 with lipids and the like.

The di- or tri(meth)acrylate of a dihydric
or higher hydric alcohol is a crosslinking agent and a
component contributing to structural stability and
increase of hardness of the copolymer obtained. Examples
10 are di(meth)acrylates of ethylene glycol, diethylene
glycol, triethylene glycol, tetraethylene glycol,
propylene glycol and butylene glycol; trimethylolpropane
tri(meth)acrylate; and the like. These compounds are
used in the range of 0.1 to 15% by weight. Besides,
15 there may be used, for example, diallyl phthalate,
diallyl isophthalate, triallyl cyanurate, triallyl
isocyanurate, divinylbenzene, bisphenol A dimethacrylate,
diethylene glycol bisallylcarbonate and the like.

As the initiator for polymerizing the above
20 components, there are used ordinary free radical-forming
reagent or initiators such as, for example, benzoyl
peroxide, lauroyl peroxide, cumene hydroperoxide,
di-tert-butyl peroxide, bis-(4-tert-butyl cyclohexyl)-
peroxydicarbonate, diisopropyl peroxydicarbonate, 2,2'-
25 azobisisobutyronitrile, 2,2'-azobis-2,4-(dimethyl-
valeronitrile) and the like. The use of a polymerization
initiator forming a radical at low temperatures is
preferable.

1 In this invention, the above mentioned monomer
 components are mixed and then poured into a mold made
 of a metal, glass, a plastic or the like, and poly-
 merization is completed in a closed condition by adopting
5 a continuous stepwise temperature raising method of
 40° to 100°C, and the polymer obtained is processed
 into a lens shape by ordinary mechanical processing
 and polishing. The oxygen-permeable hard contact lens
 thus formed is superior in stain resistance, scratch
10 resistance and hydrophilicity to conventional oxygen-
 permeable lenses mainly composed of silicone methacrylates
 and further superior in optical clarity and uniformity
 of lens. In addition, since the copolymer obtained
 according to this invention has excellent machinability
15 and polishability when the copolymer is mechanically
 processed into a lens shape, it can be easily processed
 into a desired lens dimension and a lens with excel-
 lent dimensional stability can be obtained. These
 advantages are brought about as a result of the fact
20 that superior points of each copolymerizing component
 are sufficiently utilized and thereby inferior points of
 these components are offset. Accordingly, the hard
 contact lens of this invention is very significant in
 that it is equipped with various properties not obtainable
25 with conventional oxygen-permeable hard contact lenses.

 Hereinunder, Examples of this invention are
 shown.

1 Example 1

45 Parts by weight of methyl methacrylate, 30 parts by weight of trifluoroethyl methacrylate, 15 parts by weight of tris(trimethylsiloxy)silylpropyloxy methacrylate, 5 parts by weight of methacrylic acid, 5 parts by weight of trimethylolpropane trimethacrylate and 0.3 part by weight of azobisisovaleronitrile as polymerization initiator were mixed thoroughly. The resulting mixture was placed in a high density polyethylene tube and the tube was sealed after replacing the inside gas with nitrogen. Then, the tube was subjected to heating for 24 hr in a water bath of 40°C, for 12 hr in a electric oven of 60°C and for 10 hr in the same oven increased to 100°C to copolymerize the contents. The copolymer obtained was colorless and transparent and optically uniform. Specimens were cut off the copolymer to measure its physical and other properties. As shown in Table 1, this copolymer was an oxygen-permeable material excellent in surface hardness, scratch resistance and stain resistance and good in wettability by water. Using this copolymer, a contact lens was produced by ordinary mechanical processing and polishing. In actual use, this oxygen-permeable hard contact lens gave a very good feeling of use, was difficult to get scars and had excellent durability. Further, in use over a long period of time staining of the lens surface was very minor.

1 Example 2

30 Parts by weight of methyl methacrylate,
30 parts by weight of trifluoroethyl methacrylate, 25 part
by weight of tris(trimethylsiloxy)silylpropyloxy
5 methacrylate, 10 parts by weight of methacrylic acid,
5 parts by weight of tetraethylene glycol dimethacrylate
and 0.2 part by weight of 2,2'-azobisisobutyronitrile
were mixed thoroughly. The resulting mixture was
placed in a teflon tube and sealed after replacing the
10 inside gas with nitrogen. The tube was placed in a
electric oven and heated for 26 hr at 40°C, for 16 hr
at 50°C, for 5 hr at 80°C and for 6 hr at 100°C to
complete copolymerization. The copolymer obtained was
tested for physical properties, in which it showed an
15 oxygen permeability coefficient of 14.2×10^{-10}
[cc(STP)cm/cm²·sec·cm Hg] and a contact angle of 65°
(good wettability by water). Further, a contact lens
was produced from this copolymer by mechanical processing.
The lens was superior particularly in machinability and
20 polishability. In actual use, this oxygen-permeable
hard contact lens, as compared with conventional hard
contact lenses, gave a low feeling of foreign matter.
Moreover, in use over long hours, staining of the lens
surface was very minor.

25 Examples 3 to 8

Copolymerization was conducted in the same
manner as in Examples 1 and 2 to obtain respective

1 copolymers. Contact lenses were produced by subjecting
the copolymers to mechanical processing. These lenses
were all oxygen-permeable hard contact lenses excellent
in surface hardness, wear and scar resistance, stain
5 resistance and hydrophilicity.

Table 1 shows physical and other properties
of the contact lenses of the above Examples and
Comparative Examples.

Oxygen permeability coefficient was measured
10 by the use of a Seikaken type film oxygen permeability
tester. The unit is $\text{cc(STP)cm/cm}^2\cdot\text{sec}\cdot\text{cmHg}$.

Surface hardness was shown in Knoop hardness
and pencil hardness. Pencil hardness was measured by
JIS K 5401.

15 Contact angle was measured in accordance with
the droplet method by the use of an Erma contact
anglemeter. The unit is degree.

Scratch resistance was measured by the use of
the eraser hardness testing method. A lens having very
20 few scars on the surface was rated as ◎, a lens having
few scars as o and a lens having many scars as x.

Processability is compared with those of hard
contact lenses mainly composed of methyl methacrylates.
A lens having excellent processability was rated as
25 ◎, a lens having good processability as o and a lens
having poor processability as x.

Transparency was measured by visually checking
a copolymer, a plate or a lens. Excellent transparency

1 was rated as © , good transparency as o and poor
transparency as x.

Stain resistance was measured by immersing a
sample in a liquid containing lacrima components such
5 as proteins, lipids and the like, then washing the
sample surface with water and examining stain substances
adhered to the sample surface by visual check, micro-
scopic observation and absorbance measurement at
ultraviolet wavelengths. A sample having very few
10 stains on the surface was rated as © , a sample having
slight stains as o and a sample heavily stained as x .

Examples A to C

In Table 2 there were shown physical and
other properties of (1) conventional oxygen-permeable
15 hard contact lens materials produced from methyl
methacrylate, tris(trimethylsiloxy)silylpropyloxy
methacrylate, methacrylic acid and tetraethylene
glycol dimethacrylate and (2) an oxygen-permeable
hard contact lens material produced from the above four
20 components and trifluoroethyl methacrylate as fluorine-
containing monomer. The ratios of monomer components
excluding trifluoroethyl methacrylate in Examples A,
B and C correspond to the monomer ratios in Comparative
Examples a, b and c, respectively. It is apparent
25 from Table 2 that addition of trifluoroethyl methacrylate
improved all tested properties such as oxygen per-
meability, hardness, scratch resistance, stain resistance

1 and transparency.

It is anticipated generally that addition of a fluorine-containing monomer reduces hardness and increases contact angle for water. However, contrary to
5 the expectation, it was confirmed that, by addition of a fluorine-containing monomer, the silicone methacrylate hitherto employed to enhance oxygen permeability can be used in a smaller quantity and further the uniformity of the copolymer obtained is improved whereby transparency
10 and processability do not deteriorate even if a hydrophilic monomer used to enhance contact angle and hardness, a crosslinking agent and the like are used in large quantities.

Table 1

		Parts by weight	Oxygen permeability coefficient, $\times 10^{-10}$	Hardness	
				Knoop	Pencil
Comparative Examples					
1	MMA/EDMA	98/2	0.1	20.0	2H
2	MMA/TSPM	49/51	20.1	6.8	N
3	"	79/21	2.4	10.5	HB
Examples					
1	MMA/TFEM/TSPM/MA/TMPT	45/30/15/5/5	8.9	14.1	H
2	MMA/TFEM/TSPM/MA/4G	30/30/25/10/5	14.2	12.9	H
3	MMA/PFPM/TSPM/MA/2G	35/35/20/5/5	12.8	13.2	H
4	MMA/HEIPM/TSPM/MA/4G	30/30/25/10/5	17.3	12.8	H
5	MMA/HFIPM/PMSM/MA/TMPT	40/25/13/10/12	9.6	13.6	H
6	MMA/TFEM/TSPM/TBTMSM/MA/EDMA	40/25/15/5/5/10	8.4	12.7	H
7	MMA/TFEM/TSPM/TPHESM/MA/TMPT	40/25/15/5/10/5	9.2	13.4	H
8	MMA/TBMA/TFEM/TSPM/MA/4G	20/20/35/10/5/10	10.3	11.2	F

- Cont'd -

MMA: Methyl methacrylate, TBMA: Tert-butyl methacrylate,
 TFEM: Trifluoroethyl methacrylate PFPM: Pentafluoropropyl methacrylate,
 HFIPM: Hexafluoroisopropyl methacrylate,
 TSPM: Tris(trimethylsiloxy)silylpropyloxy methacrylate,

Table 1 (Cont'd)

Contact angle for water, degree	Scratch resistance	Process- sability	Stain resistance	Trans- parency
65	⊙	⊙	○	⊙
78	x	x	x	x
76	x	○	x	○
65	⊙	⊙	⊙	⊙
65	⊙	⊙	⊙	⊙
67	⊙	⊙	⊙	⊙
68	⊙	⊙	⊙	⊙
68	⊙	⊙	⊙	⊙
66	⊙	⊙	⊙	○
66	⊙	⊙	⊙	○
67	○	○	⊙	○

PMS: Pentamethyldisiloxanymethyl methacrylate,
 TBTMSM: Tert-butyltetramethyldisiloxanylethyl methacrylate,
 TPHEM: Triphenyldimethyldisiloxanymethyl methacrylate,
 MA: Methacrylic acid, EDMA: Ethylene glycol dimethacrylate,
 2G: Diethylene glycol dimethacrylate, 4G: Tetraethylene glycol dimethacrylate,
 TMPT: Trimethylolpropane methacrylate

Table 2

		Parts by weight	Oxygen permeability coefficient, $\times 10^{-10}$	Hardness	
				Knoop	Pencil
a	Comparative Examples MMA/TSPM/MA/4G	47/35/12/6	10.1	9.7	HB
b	MMA/TSPM/MA/TMPT	47/35/12/6	9.2	11.5	F
c	"	57/29/7/7	7.9	10.8	HB
A	Examples MMA/TFEM/TSPM/MA/4G	40/15/30/10/5	13.8	11.8	F
B	MMA/TFEM/TSPM/MA/TMPT	40/15/30/10/5	12.5	13.3	H
C	"	40/30/20/5/5	10.5	13.0	H

- Cont'd -

Table 2 (Cont'd)

Contact angle for water, degree	Scrach resistance	Proces- sability	Stain resistance	Trans- parency
67	x	x	x	x
66	o	x	x	x
67	x	x	x	x
66	o	o	⊙	⊙
66	⊙	⊙	⊙	⊙
65	⊙	⊙	⊙	⊙

WHAT IS CLAIMED IS:

1. An oxygen-permeable hard contact lens made of an oxygen-permeable transparent high molecular material produced by polymerizing in a mold a composition composed of 30 to 50% by weight of an alkyl (meth)acrylate, 10 to 40% by weight of a fluorine-containing monomer, 10 to 35% by weight of a silicone (meth)acrylate, 5 to 15% by weight of an unsaturated carboxylic acid having at least one carboxylic group in the molecule and 0.1 to 15% by weight of a di- or tri(meth)acrylate of a dihydric or higher hydric alcohol by raising a temperature continuously or stepwise from 40° to 100°C.
2. An oxygen-permeable hard contact lens according to Claim 1, wherein the alkyl (meth)acrylate is at least one member selected from the group consisting of methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, iso-propyl (meth)acrylate, n-butyl (meth)acrylate, iso-butyl (meth)acrylate and tert-butyl (meth)acrylate.
3. An oxygen-permeable hard contact lens according to Claim 1 or 2, wherein the fluorine-containing monomer is at least one perfluoroalkylmethyl (meth)acrylate selected from the group consisting of trifluoroethyl (meth)acrylate, pentafluoroisopropyl (meth)acrylate, heptafluorobutyl (meth)acrylate and hexafluoroisopropyl (meth)acrylate.

4. An oxygen-permeable hard contact lens according to any of Claims 1 to 3, wherein the silicone (meth)acrylate is at least one member selected from the group consisting of tris(trimethylsiloxy)silylpropyloxy (meth)acrylate, triphenyldimethyldisiloxanylmethyl (meth)acrylate, pentamethyldisiloxanylmethyl (meth)acrylate, tert-butyltetramethyldisiloxanylethyl (meth)acrylate and methyldi(trimethylsiloxy)silylpropylglyceryl (meth)acrylate.
5. An oxygen-permeable hard contact lens according to any of Claims 1 to 4, wherein the unsaturated carboxylic acid having at least one carboxylic group in the molecule is acrylic acid or methacrylic acid.
6. An oxygen-permeable hard contact lens according to any of Claims 1 to 5, wherein the di- or tri(meth)acrylate of a dihydric or higher hydric alcohol is at least one monomer selected from the group consisting of (a) di(meth)acrylates of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol and butylene glycol and (b) trimethylolpropane tri(meth)acrylate.

INTERNATIONAL SEARCH REPORT

0114894

International Application No. PCT/JP83/00237

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. ³ G02C 7/04		
II. FIELDS SEARCHED		
Minimum Documentation Searched ²		
Classification System	Classification Symbols	
I P C	G02C 7/04, C08F 220/10	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ³		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁴		
Category ⁵	Citation of Document, ⁶ with indication, where appropriate, of the relevant passages ⁷	Relevant to Claim No. ⁸
Y	JP,A, 47-56532 (E.I. Du Pont de Nemours and Company) 27. February. 1973, (27. 02. 73)	1 - 6
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Y	JP,A, 54-66853 (Toyo Contact Lens Kabushiki Kaisha) 29. May. 1979, (29. 05. 79)	1 - 6
Y	JP,A, 54-118455 (Polymer Technology Corp.) 13. September. 1979, (13. 09. 79)	1 - 6
Y	JP,A, 55-15110 (Toyo Contact Lens Kabushiki Kaisha) 2. February. 1980, (02. 02. 80)	1 - 6
Y	JP,A, 55-102613 (George F. Tsuetaki) 6. August. 1980, (06. 08. 80)	1 - 6
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⁹ Special categories of cited documents: ¹⁰ ¹¹ "A" document defining the general state of the art which is not considered to be of particular relevance ¹² "E" earlier document but published on or after the international filing date ¹³ "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) ¹⁴ "O" document referring to an oral disclosure, use, exhibition or other means ¹⁵ "P" document published prior to the international filing date but later than the priority date claimed ¹⁶ "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention ¹⁷ "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step ¹⁸ "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art ¹⁹ "Z" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²⁰	Date of Mailing of this International Search Report ²¹	
October 14, 1983 (14. 10. 83)	October 24, 1983 (24. 10. 83)	
International Searching Authority ²²	Signature of Authorized Officer ²³	
Japanese Patent Office		